

THE INFRARED ABSORPTION SPECTRA OF ACETYLENE,
ETHYLENE, AND ETHANE

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BY

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THE INFRARED ABSORPTION SPECTRA OF ACETYLENE, ETHYLENE AND ETHANE

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ABSTRACT

The spectra of acetylene, ethylene and ethane have been investigated with gratings in the region between 2 and 15μ . Each gas shows a more or less characteristic type of structure for its vibrational-rotational bands. The three main absorption regions of acetylene have been resolved into individual lines which are alternately intense and faint. These lines have the same average spacing in the three bands. The band at 13.7μ shows a strong unresolved Q branch, while the bands at 7.5 and 3.0μ lack evident Q branches. The two minor absorption regions of acetylene have also been investigated. The molecular moment of inertia has been computed from the spacing of the fine structure of the principal acetylene bands. The moment of inertia has also been computed from the classical theory on the assumption of a linear molecular model. The values obtained by the two methods are in agreement.

For ethylene, seven regions of absorption have been investigated. Two of these have been resolved into individual lines, with a strong Q branch present in one case and absent in the other. Four of the remaining regions reveal envelope of an identical type, which is characterized by a sharp Q branch together with P and R branches. The bands found in the region of 2.3μ apparently lack Q branches. This latter group has been partially resolved.

The main absorption regions of ethane reveal bands, each consisting of a single succession of absorption maxima. The spacing of these maxima is different for each of the bands, but the structure obtained is for the most part of a regular nature.

INTRODUCTION

Our knowledge of the molecular structure of gases has been greatly advanced in recent years by the application of quantum mechanics to the vibrational-rotational bands in the infra-red region. The general shapes of the band envelopes, the presence or absence of Q branches, the frequency spacings and the relative intensities of the absorption lines are all questions to which theoretical interest is attached. The quantum mechanics has made considerable progress in the diatomic case, and its extension to the more general problem of the polyatomic molecule is engaging serious attention in the field of theoretical physics.

It was with the view of extending our knowledge of the fine structure of the infra-red bands and hence opening the way to their theoretical interpretation in terms of the quantum theory, that the present work was undertaken.

Preliminary investigations, reported in a previous paper,¹ were devoted to the absorption bands of several compounds in the region of 3.4μ . Of the many substances considered, the lower hydrocarbons offered the most promise of yielding relatively simple and resolvable fine structure. The scope of the present investigation has therefore been limited to the examination under high dispersion of the vibrational-rotational bands of acetylene (C_2H_2), ethylene (C_2H_4) and ethane (C_2H_6) in the spectral region from 2μ to 15μ . Most of these bands have now been resolved and show fine structure having a regular nature. In some cases the regularities obtained are of a type not previously observed in vibrational-rotational bands.

The spectral region under consideration in the present work has been examined by Coblentz with a prism spectrometer. The results obtained in this manner for acetylene, ethylene, and ethane are included in his extensive treatise on infra-red absorption.² As a matter of convenience, the curves presented by Coblentz have been redrawn so as to show absorption increasing upwards, and are included herein as a part of Figure 1. The absorption regions for acetylene have been re-explored with a prism spectrometer by Burmeister³ whose readings extended as far as 22μ . No indications of absorption were reported for the region beyond 15μ , but at 2.5μ Burmeister located a minor absorption maximum which did not appear in Coblentz' curves.

All of the absorption regions for the three gases have been examined under high dispersion in the present investigation, with the exception of the minor absorption maximum for ethylene at 4.3μ . Investigation of this maximum was unfeasible, because of the strong overlying absorption of carbon dioxide in the atmosphere.

From a comparison of the frequencies of the absorption maxima for acetylene and ethylene as given by Burmeister and Coblentz respectively, Hettner⁴ has suggested that certain of the bands might be explained as harmonics of a fundamental vibration frequency. Such

¹ Meyer, C. F., Bronk, D. W. and Levin, A., J.O.S.A. & R.S.I. 15, pp. 257-266; 1927.

² Coblentz, W. W., Publications of the Carnegie Institution of Washington, 35; 1905.

³ Burmeister, W., Verhandlungen der Deutschen Physikalischen Gesellschaft, 15, pp. 589-612; 1913.

⁴ Hettner, G., ZS. für Physik, 1, pp. 345-354; 1920.

an assumption is quite logical on the basis of the prism data alone. The examination of the bands under high dispersion, however, reveals important differences in the structure of the so-called fundamental and harmonics which make such a classification exceedingly doubtful.

APPARATUS

The grating spectrometer used in this work is of a type similar to that employed by previous investigators,⁵ and therefore will not be described here in detail. Modifications of an important nature, however, lead to a high degree of sensitivity of the recording apparatus and hence allow investigation with a grating to a greater wave-length than has been previously reached. As a further consequence of the increased sensitivity, it has been possible to reduce the slit widths considerably and thus obtain improved definition. In the following discussion, only the important features of the apparatus will be considered.

The radiant energy from a Nernst glower is passed through a fore-prism of rock salt which serves as a monochromator. This prism is necessary in order to prevent the overlapping of spectral orders. The energy passes from the monochromator through the absorption cell containing the gas to be studied, and then falls upon the slit of the spectrometer. The focal length of the spectrometer is 100 centimeters. The gratings used are all large Michigan echelettes, ruled by Dr. Barker. A grating ruled with 7200 lines per inch (2834 lines per cm) on a copper-nickel surface was found to be most effective for the region between 2μ and 4μ . From 4μ out to the neighborhood of 8μ , the best results were obtained with a grating having 2880 lines per inch (1134 lines per cm) on an aluminum surface. The region from 8μ to 15μ was made accessible by a grating of 1440 lines per inch (567 lines per cm) ruled on a tin surface.

The detecting system consists of a vacuum thermocouple, a Moll thermal relay and a Leeds and Northrup high-sensitivity galvanometer of the D'Arsonval type. The vacuum thermocouple was constructed according to the method of Dr. A. H. Pfund⁶ and was furnished with a calcium evacuator.⁷

The absorption cell is equipped with rock salt windows and can be used effectively throughout the entire spectral region from 2μ to 15μ . Compensating windows were found to be unnecessary, as the diminution

⁵ Sleator, W. W., *Astrophysical Journal*, 48, pp. 125-143; 1918.

⁶ Pfund, A. H. *Physikalische ZS.*, 13, pp. 870-873; 1912.

⁷ Coblentz, W. W. *J.O.S.A. & R.S.I.*, 5, pp. 356-362; 1921.

of energy due to the rock salt windows can be satisfactorily taken into account. The length of the absorption cell can be varied from 1 mm to 20 cm.

Between 2μ and 3μ , the dispersion of the rock salt prism was found to be too low to eliminate overlapping of the spectral orders. Consequently an asphaltum filter was used for work in this region. This filter is practically opaque to energy as far as 1.5μ , while it transmits a major portion of the energy from 2μ to 3μ . Hence it serves its purpose quite admirably.

EXPERIMENTAL PROCEDURE

The absorption cell was adjusted to a convenient length and sealed. Thereupon it was filled with the gas which had been passed through a drying chamber containing concentrated sulphuric acid. For a majority of the runs the length of the cell was 8 centimeters. When working in regions of intense absorption, the effective gas content of the cell was decreased to a suitable value by diluting with air.

The percentage of absorption due to the gas at any given position of the grating was obtained from repeated galvanometer deflections which were observed on opening and closing the shutter with the cell in the beam and with the cell out of the beam. In investigating a region of absorption, an exploratory run was first taken point by point, the successive positions of the grating being separated by intervals of five minutes of arc. This preliminary run was carried well beyond the limits of the region as shown by the prism curves of Coblentz. The main absorption region thus determined was then examined more fully with narrower slits and at smaller intervals.

The calibration of the 7200 line grating was based upon repeated observations on the -3 and -4 lines of hydrogen chloride, whose positions have been determined by Colby, Meyer and Bronk.⁸ These same standards served for calibrating the 2880 line grating, but in this case the calibration was supplemented by visual observations on the green mercury line. The 1440 line grating was calibrated from the first and second order images of the sharp Q branch of ethylene at 5.292μ , as previously obtained with the 2880 line grating. The latter calibrations were confirmed by some direct measurements made by Dr. Barker on the comparator.

⁸ Colby, W. F., Meyer, C. F. and Bronk, D. W. *Astrophysical Journal*, 57, pp. 7—19: 1923.

DISCUSSION OF RESULTS

An assembly of the results is presented in Fig. 1. In this are included the prism curves obtained by Coblenz, and associated with each region of absorption is a miniature graph showing the nature of the fine structure revealed in the present work.

A typical curve for each region investigated is shown in the figures numbered 2 to 13. These curves were originally plotted with absorption percentages as ordinates and with settings of the spectrometer circle as abscissae. The scale of circle settings has, however, been replaced in the figures by corresponding scales of wave-lengths, in μ , and of wave-numbers per millimeter.

For purposes of reference, arbitrary numbers are assigned to the individual lines in the absorption bands. Each line which has been confirmed by repeated observations is given a number. This number is indicated by a scale placed slightly below the curve in each figure. Scale marks have also been placed beneath some of the minor maxima which have not been confirmed, and which may be due to observational error. Moreover, scale marks have occasionally been inserted where there are no maxima at all; this has been done either for convenience in making out the scale, or to allow numbers for lines which may be disclosed by future investigation. In determining line numbers, the reader should take account of the number of marks between adjacent numbered positions of the scale; e.g. in Fig. 11, there are four marks between Nos. 270 and 280. The absorption lines above these marks consequently carry the numbers 272, 274, 276, and 278. There is no mark corresponding to line No. 277, but it is readily ascertained to be the faint line lying between lines 276 and 278.

Numbers are also assigned to the maxima of the envelopes of the *P*, *Q*, and *R* branches. These maxima cannot be located with a high degree of precision. Consequently for the branches which have been resolved into lines, the maximum of the envelope may with sufficient accuracy be taken as coincident in position with one of the lines. When a branch is not resolved into lines, the plotted observations yield directly the envelope of the branch, and a number is assigned to the maximum of the plotted envelope.

Table 1 gives information regarding the experimental conditions under which the absorption curves were obtained. It may be noted that the slit width, expressed in spectral range, varies from 164A to 8A. In regions where the amount of energy available permitted the use of narrow slits, a high order of definition was attained.

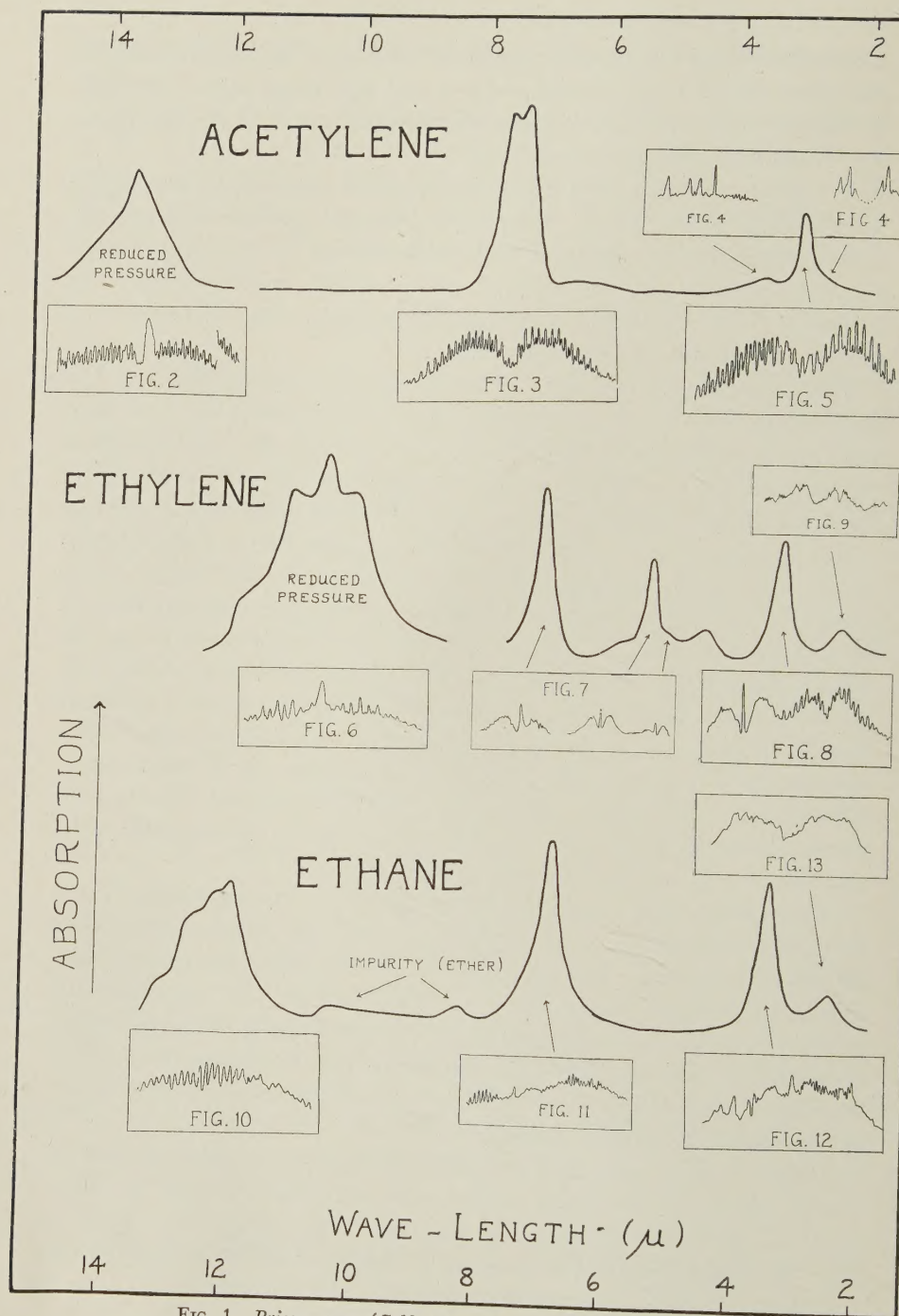


FIG. 1. Prism curves (Coblentz), and miniature grating curves.

TABLE 1. *General information regarding conditions under which following tabular data were obtained.*

Gas	Region	Grating Lines/cm	Interval of readings		Slit width		Cell length, cm
			Min.	A. U.	mm	A. U.	
Acetylene	13.7 μ	567	1	94	1.00	160	4 Partly Filled
	7.5	1134	1	46	0.75	59	8 " "
	3.7	2835	1	17	0.50	15	8 Filled
	3.0	2835	1/4	5	0.25	8	8 Partly Filled
Ethylene	10.5 μ	567	1	98	0.80	134	8 Partly Filled
	6.9	1134	1/2	23	0.75	60	6 " "
	5.2	1134	1	49	0.50	42	8 " "
	4.9	1134	1	49	0.50	42	8 Filled
	3.3	2835	1	18	0.50	16	8 Partly Filled
	2.3	2835	1	19	0.50	16	8 Filled
	Lines 656-676	2835	1/2	10	0.25	8	8 Filled
Ethane	12.2 μ	567	1	96	1.00	164	3.2 Filled
					0.50	82	3.2 "
	7.5	1134	1	46	0.75	59	8 Partly Filled
	6.8	1134	1	47	0.75	60	8 " "
	3.4	2835	1/2	9	0.50	16	8 " "
	2.4	2835	1	19	0.50	16	8 Filled

The following tables numbered 2 to 12, give the wave-numbers of the absorption lines and the wave-number differences between adjacent lines. The wave-numbers corresponding to minor maxima in the curves are included in the tables only when these minor maxima have been confirmed by repetition. The table numbers have been made to correspond throughout with the figure numbers, so that the data for any given region of absorption may be found under the same number in both tabular and graphical form. The results obtained for each of the three gases investigated will now be presented in detail.

ACETYLENE

The acetylene gas was obtained from a Prest-o-lite cylinder, and was dried by passing through concentrated sulphuric acid. The principal regions exhibit very regular structure and evidently contain no lines due to impurity in the gas.

The prisms curves of Coblentz show three main absorption regions. Each region has been examined and its fine structure revealed. The structure obtained is remarkably simple and regular, in view of the

TABLE 2. *Acetylene—Region of 13.7 μ .*

Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$
130	684.71		141	710.44		155	741.08		166	766.96	
		2.16			2.30			2.53			2.15
1	6.87		2	2.74		6	3.61		7	9.11	
		2.40			2.57			2.05			2.42
2	9.27		3	5.31		7	5.66		8	771.53	
		2.41			1.93			2.42			2.46
3	691.68		4	7.24		8	8.08		9	3.99	
		2.22			2.68			2.28			2.12
4	3.90		5	9.92		9	750.36		170	6.11	
		2.18			2.21			2.28			2.49
5	6.08		6	722.13		160	2.64		1	8.60	
		2.54			2.47			2.70			2.13
6	8.62		7	4.60		1	5.34		2	780.73	
		2.42			1.52			2.25			2.40
7	701.04		8	6.12		2	7.59		3	3.13	
		2.30						2.20			2.30
8	3.34		150	730.35		3	9.79		4	5.43	
		2.31						2.35			2.48
9	5.65		2	3.61		4	762.14		5	7.91	
		2.37			2.72			2.50			2.07
140	8.02		3	6.33		5	4.64		6	9.98	
		2.42			2.29			2.32			
			4	8.62							
					2.46						

	Coinciding with line no.	Wave number $\nu(cm^{-1})$	$\Delta\nu$
Maximum of Envelope, P Branch	140	708.02	
" " " Q "	150	730.35	22.33
" " " R "	160	752.64	22.29

complexity of the acetylene molecule, and there is great promise that it will lend itself to theoretical treatment. The two minor absorption

maxima located by Burmeister at 3.8μ and 2.5μ have also been further resolved.

Region of 13.7μ (Fig. 2, Table 2): The wide and intense absorption maximum shown by the prism curve resolves itself into a band consisting of *P*, *Q*, and *R* branches. The *P* and *R* branches consist of two sets of absorption lines of alternately high and low intensity, this alternation being most strongly marked in the *R* branch on the right of the figure. The detached portion of curve shown here represents observations taken with more gas in the cell.

In the *P* branch the alternation of intensities is again well marked in lines 130 to 142. Perturbations in the spacing and intensity of lines numbered 143 to 146 were at first attributed to experimental error.

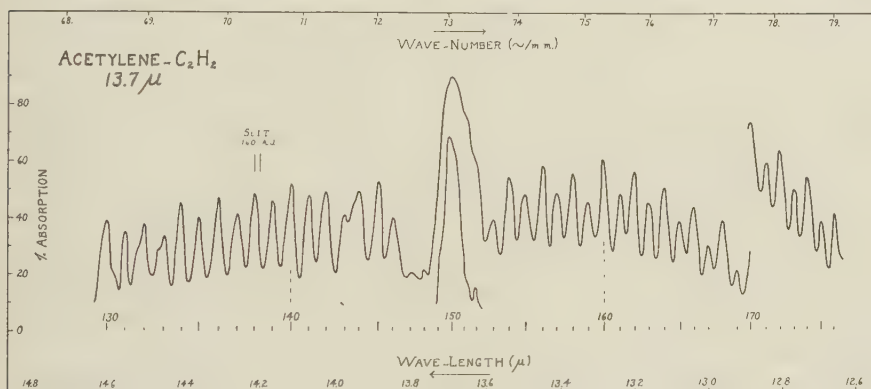


FIG. 2.

Repeated observations over this region, however, have confirmed the perturbations shown. The irregularities which are apparent at the left end of the *P* branch can, on the other hand, be attributed to observational error. The energy falls off very rapidly in this region due to absorption by the carbon dioxide of the atmosphere.

There is no convergence in either the *P* or the *R* branch, the average spacing of the lines being 2.35 cm^{-1} . The small deviations from this value shown in the table are due to experimental error in locating the positions of individual lines. If the above value of the average spacing is applied to the central portion of the band, it is apparent that there are just nine spacings between lines 145 and 155. Due to the absence of convergence in the band, this determination can be definitely made. Hence it is seen that the strong lines in the *R* branch form a regular sequence with the weak lines in the *P* branch, and vice versa.

Repeated runs taken over the Q branch with decreasing gas content show a progressive shift of the branch toward lower wave-numbers. This indicates that the series of lines constituting the Q branch is degraded toward higher wave-numbers.

An attempt has been made to set forth the three positions of maximum absorption in the envelope of the band. These positions are of importance as they lead directly to values of $\bar{\nu}_r$, the "most probable frequency of rotation" which enters into classical theory. An exact determination is difficult, particularly for the P branch due to the flatness of its envelope. The mean value of 22.3 cm^{-1} , representing the authors' determination of $\bar{\nu}_r$, can be applied in the classical formula⁹ for a linear molecular model,

$$I = \frac{RT}{4\pi^2 N c^2 \bar{\nu}_r^2} = \frac{1140 \times 10^{-39}}{\bar{\nu}_r^2},$$

giving a resultant moment of inertia $I = 2.3 \times 10^{-39} \text{ gr-cm}^2$.

On the basis of the quantum theory, the moment of inertia of the molecule is given approximately by the formula

$$I = \frac{h}{4\pi^2 c(\Delta\nu)}.$$

Applying the average spacing of the lines, $\Delta\nu = 2.35 \text{ cm}^{-1}$, we obtain for the acetylene molecule $I = 2.4 \times 10^{-39} \text{ gr-cm}^2$. This compares re-

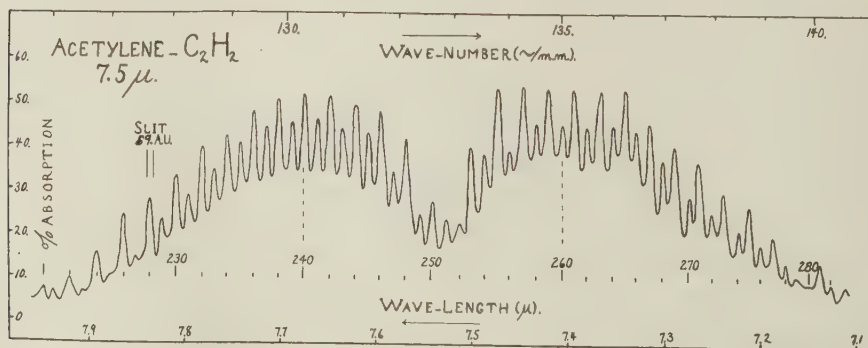


FIG. 3.

markably well with the value given above by the classical formula on the assumption of a linear molecular model.

⁹ Eucken, A. ZS. für Electrochemie, 26, pp. 377-383; 1920.

TABLE 3. *Acetylene—Region of 7.5μ.*

Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$
220	1258.05		236	1293.96		252	1330.83		268	1369.58	
		1.68			2.25			2.40			2.20
1	59.73		7	96.21		3	33.23		9	71.78	
		2.79			2.24			2.45			2.41
2	62.52		8	98.45		4	35.68		270	74.19	
		2.37			2.35			2.38			2.50
3	64.89		9	1300.80		5	38.06		1	76.69	
		2.14			2.34			2.28			2.58
4	67.03		240	03.14		6	40.34		2	79.27	
		2.33			2.28			2.41			2.23
5	69.36		1	05.42		7	42.75		3	81.50	
		2.16			2.30			2.49			2.68
6	71.52		2	07.72		8	45.24		4	84.18	
		2.22			2.18			2.40			2.46
7	73.74		3	09.90		9	47.64		5	86.64	
		2.23			2.30			2.60			2.35
8	75.97		4	12.20		260	50.24		6	88.99	
		2.18			2.26			2.21			2.39
9	78.15		5	14.46		1	52.45		7	91.38	
		2.31			2.27			2.53			2.56
230	80.46		6	16.73		2	54.98		8	93.94	
		2.28			2.25			2.35			2.18
1	82.74		7	18.98		3	57.33		9	96.12	
		2.19			2.37			2.59			
2	84.93		8	21.35		4	59.92		281	1400.91	
		2.22			2.42			2.29			
3	87.15		9	23.77		5	62.21		2	03.00	
		2.24			2.49			2.31			
4	89.39		250	26.26		6	64.52		3	06.00	
		2.28			2.31			2.61			
5	91.67		1	28.57		7	67.13				
		2.29			2.26			2.45			

	Coinciding with line no.	Wave number ν /cm	$\Delta\nu$
Maximum of Envelope, P Branch	240	1303.14	23.12
Minimum of Envelope; Band Center		1326.26	23.98
Maximum of Envelope, R Branch	260	1350.24	

Region of 7.5μ (Fig. 3, Table 3): In this band the *P* and *R* branches again consist of sharply defined absorption lines which are alternately strong and weak. The alternation of intensities is well marked throughout both branches. It may be noted that the even numbered lines from 220 to 250 (the strong lines of the *P* branch) form a regular sequence with the even numbered lines from 252 to 282 (the weak lines of the *R* branch). Similarly, the weak lines of the *P* branch form a regular sequence with the strong lines of the *R* branch. It is possible that one of the lines near the center of the band represents a faint *Q* branch.

Computations can be made of the mid-positions between strong lines which are symmetrically placed in the *P* and *R* branches. The values thus obtained range progressively from 1327.3 cm^{-1} (from lines 248 and 253) to 1329.5 cm^{-1} (from lines 220 and 281). This shift is sufficient to yield a sure indication of convergence toward lower wave-numbers. The type of convergence found here is extraordinary in infra-red bands.

The average displacement of the maxima of the envelopes of the *P* and *R* branches from the approximate center of the band is taken as the $\bar{\nu}_r$ in the classical formula cited above. This value, $\bar{\nu}_r = 23.5\text{ cm}^{-1}$ leads to a determination of the molecular moment of inertia $I = 2.1 \times 10^{-39}\text{ gr-cm}^2$. These results are in close accord with those obtained for the 13.7μ band.

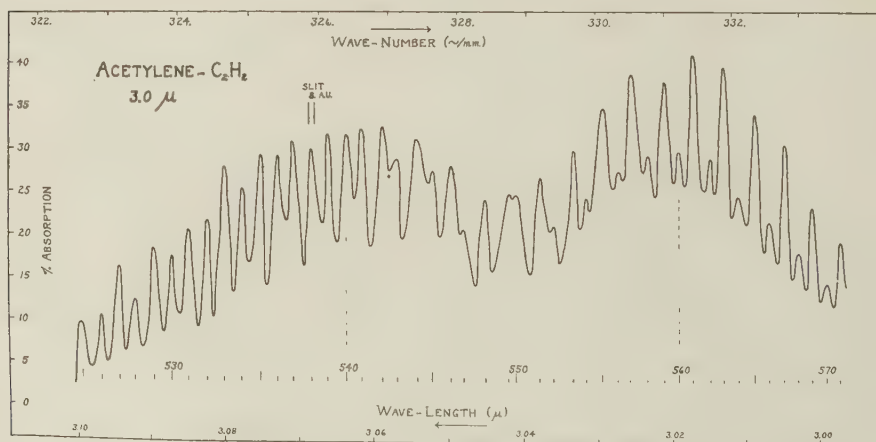


FIG 5.

The spacing of the fine structure near the center of the band has an average value of $\Delta\nu = 2.35\text{ cm}^{-1}$ (from lines 235-245 and 255-265). This, when substituted in the formula of the quantum theory, again gives the value $I = 2.4 \times 10^{-39}\text{ gr-cm}^2$.

Region of 3.0 μ (Fig. 5, Table 5): The absorption curve shown in the figure represents the fifth complete run taken over this region. The gas content was readjusted and the slit widths and the reading

TABLE 5. *Acetylene—Region of 3.0 μ .*

Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$
525	3226.04		537	3256.15		549	3287.07		561	3314.18	
		2.81			2.70			1.17			2.44
6	28.85		8	58.85		550	88.24		2	16.62	
		2.62			2.26			3.16			1.96
7	31.47		9	61.11		1	91.40		3	18.58	
		2.24			2.54			2.17			2.20
8	33.71		540	63.65		2	93.57		4	20.78	
		2.73			2.30			3.11			2.30
9	36.44		1	65.95		3	96.68		5	23.08	
		2.50			3.01			1.90			2.12
530	38.94		2	68.96		4	98.58		6	25.20	
		2.47			2.07			2.25			2.31
1	41.41		3	71.03		5	3300.83		7	27.51	
		2.52			2.81			2.21			2.05
2	43.93		4	73.84		6	03.04		8	29.56	
		2.55			2.30			1.93			2.06
3	46.48		5	76.14		7	04.97		9	31.62	
		2.44			2.54			2.35			2.23
4	48.92		6	78.68		8	07.32		570	33.85	
		2.62			1.91			2.46			1.89
5	51.54		7	80.59		9	09.78		1	35.74	
		2.43			3.00			2.17			
6	53.97		8	83.59		560	11.95				
		2.18			3.48			2.23			

	Coinciding with line no.	Wave number ν /cm	$\Delta\nu$
Maximum of Envelope, P Branch	540	3263.65	
Minimum of Envelope; Band Center		3287.95	24.30
Maximum of Envelope, R Branch	560	3311.95	24.00

intervals were decreased after each of the successive runs. The data presented here represent the culmination of these trials which apparently employs the ultimate resolution of which the apparatus is capable.

The band in this region resembles the 7.5μ band in some respects and the 13.7μ band in others. The absence of a pronounced Q branch constitutes a resemblance to the former, while there are resemblances to the latter in the intensity variations in the P branch. The connection between the strong and weak series of lines is obscured by the convergence which exists in this band. The lines are found to converge in the direction of higher wave-numbers. This is shown by the fact that the mid-position, as computed from corresponding pairs of lines, shifts progressively from 3287.7 cm^{-1} (from lines 549 and 550) to 3284.7 cm^{-1} (from lines 528 and 571). This is the type of convergence usually found in vibrational-rotational bands, and is opposite to that of the 7.5μ band.

The value of $\bar{\nu}_r$ computed¹⁰ from the maxima of the envelope is 24.1 cm^{-1} . A value of the moment of inertia $I = 2.0 \times 10^{-39}\text{ gr-cm}^2$ is thus obtained, which is quite consistent with previous computations from the classical formula for a linear molecular model.

The average spacing of the lines is $\Delta\nu = 2.34\text{ cm}^{-1}$ (from lines 535-545 and 555-565). This leads to a moment of inertia $I = 2.4 \times 10^{-39}\text{ gr-cm}^2$, which is identical with the previous values obtained from the formula of the quantum theory.

Regions of 3.7μ and 2.5μ (Fig. 4, Table 4): For both of these regions of relatively weak absorption, the 8 cm cell was completely filled with gas at atmospheric pressure. The curves obtained are included in the

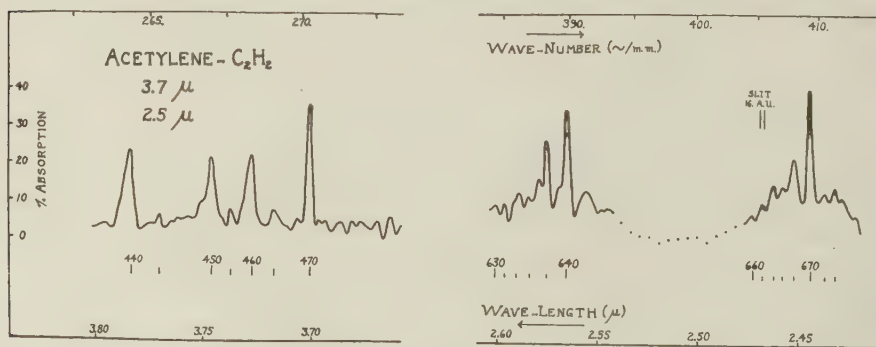


FIG. 4.

one figure. Due to the wide separations between the absorption maxima, it is probable that these may be explained as individual Q branches.

The positions of the four prominent maxima for the 3.7μ region have been calculated and are included in the table. Little weight is attached

¹⁰ The doublet separation is 48.3 cm^{-1} . A value of 41.1 cm^{-1} was given in a recent publication (see footnote 1). The latter value was obtained from an unresolved curve.

to the slight irregularities in the absorption curve occurring between these maxima, as they may be due in part to observational error. The region actually covered in the run at one minute intervals of arc extended to 2830 cm^{-1} , without revealing any important maxima other

TABLE 4. *Acetylene—Regions of 3.7μ , 2.5μ .*

Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$
440	2643.2	26.5	638	3882.3	15.6
450	2669.7		640	3897.9	
460	2683.0	13.3	668	4077.6	14.4
470	2702.2	19.2	670	4092.0	

than those shown. In the other direction, additional observations were taken at five minute intervals to 2500 cm^{-1} ; but no further indications of absorption were noted.

The fine structure obtained in the 2.5μ region reveals signs of regularity. Two distinct regions of absorption are noted here in the vicinities of 2.45μ and 2.55μ respectively, a marked resemblance existing between these two bands. Tabulation has been made of the positions of the four most prominent maxima, although several of the weaker ones also undoubtedly represent real lines. The run taken over the central portion of the curve at $2\frac{1}{2}$ minute intervals of arc is indicated in the figure by individual points. No indications of absorption are revealed here over a comparatively wide range.

The supposition advanced by Hettner (*loc. cit.*), that the 3.7μ and 2.5μ bands are harmonic with the 7.5μ band, is not confirmed by the fine structure obtained for the separate bands. In fact it is hardly conceivable that the apparent differences between the so-called fundamental and harmonics can be reconciled. Final conclusions will not, however, be drawn in this paper.

The structure obtained in these minor regions does not obviously form a part of the same spectrum which has been obtained in the principal regions. The possibility that the minor regions are due to an impurity must, therefore, be considered. But, in view of the work of Coblenz and Burmeister, it is improbable that they are due to impurity.

ETHYLENE

The ethylene was obtained from the Ohio Chemical and Manufacturing Company. The chemical analysis given by the manufacturers shows a purity of more than 99.5 per cent, the impurities listed being nitrogen, oxygen and methane. The amount of the latter impurity present is given as 0.02 per cent.

The four principal regions of absorption, indicated by Coblenz at 10.5 , 6.9 , 5.3 and 3.3μ respectively, have all been examined. The smaller maximum shown at 2.3μ has also been investigated and fine structure obtained. At 4.9μ there has been found a faint band of which slight indications appear on Coblenz' curve. Small protuberances on the prism curve which were tabulated by Coblenz at 11.8μ and 5.8μ have shown no fine structure, although slight general absorption exists in these regions. The minor absorption maximum at 4.3μ has not been investigated, as the available energy in this region is too low, due to the strong absorption of the carbon dioxide of the atmosphere.

Region of 10.5μ (Fig. 6, Table 6): The intense central maximum at 950 cm^{-1} , of which Coblenz' curve shows evidence, undoubtedly represents a *Q* branch. The interpretation of the remaining portions of the band as *P* and *R* branches is not, however, quite certain. The

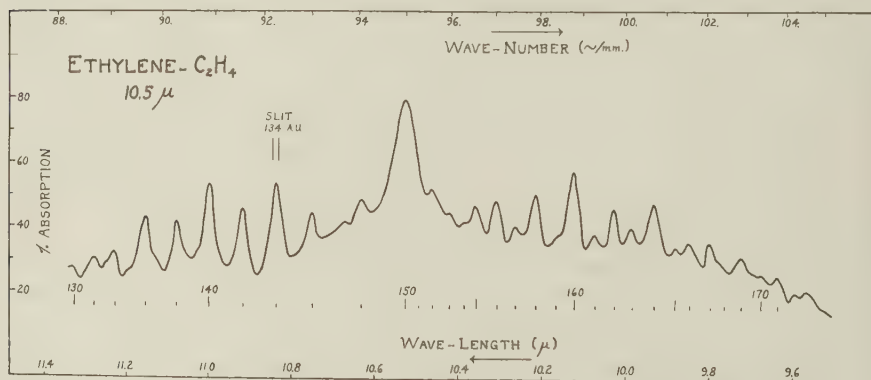


FIG. 6.

entire band has been completely examined several times, and the outstanding characteristics of the curve may safely be taken as real. That is, intensity relations for the lateral maxima which appear in the figure are repeated in various measurements, and the fainter lines lying between the more intense ones are recurrent in the region to the right of the central maximum. Of the faint lines lying near the center of

the band, only those are tabulated whose positions have been confirmed by additional runs.

The spacing of the lines in the *P* branch varies progressively from 6.05 to 7.41 cm^{-1} (from lines numbered 136 to 146). The intense lines in the *R* branch, bearing the even numbers from 156 to 164, show a

TABLE 6. *Ethylene—Region of 10.5 μ .*

Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$
134	890.51		148	940.34		158	978.90		164	1006.80	
		6.07						4.91			5.01
6	896.58		150	949.67		9	983.81		5	1011.81	
		6.05						3.82			3.72
8	902.63		2	955.46		160	987.63		6	1015.53	
		6.33						4.89			5.01
140	908.96		5	965.26		1	992.52		7	1020.54	
		6.77			4.85			4.72			
2	915.73		6	970.11		2	997.24		9	1028.30	
		6.94			4.21			4.00			
4	922.67		7	974.32		3	1001.24		171	1037.33	
		7.41			4.58			5.56			
6	930.08										

	Coinciding with line no.	Wave number ν/cm	$\Delta\nu$
Maximum of Envelope, P Branch	140	908.96	
" " " Q "	150	949.67	40.71
" " " R "	160	987.63	37.96

more irregular spacing which varies between the limits 8.73 and 9.61 cm^{-1} . The band as a whole shows a doublet spacing of 78.7 cm^{-1} ($2\bar{\nu}_r$), which is considerably greater than that found in the acetylene bands.

Regions of 6.9, 5.3, and 4.9 μ (Fig. 7, Table 7): The absorption bands for these three regions have all been included in a single figure, due to their marked resemblances in structure. Each consists of *P*, *Q*, and *R* branches, the *Q* branch being in every case sharp and well pronounced. The doublet spacings for the three bands are apparently the same, as

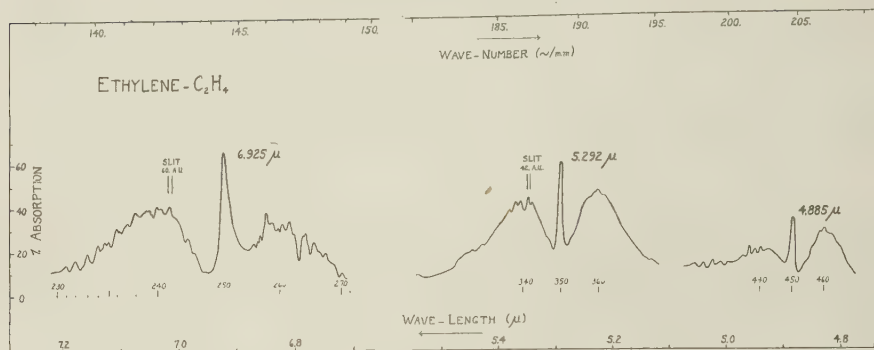


FIG. 7.

TABLE 7. Ethylene—Regions of 6.9, 5.3, 4.9μ.

Line no.	Wave number ν/cm	$\Delta\nu$
231	1389.5	3.2
232	1392.7	
233	1396.7	
234	1400.2	3.5

	Coinciding with line no.	Wave number (ν/cm)	$\Delta\nu$
Maximum of Envelope, <i>P</i> Branch	240	1420.8	23.1
" " " <i>Q</i> "	250	1443.9	
" " " <i>R</i> "	260	1464.9	
Maximum of Envelope, <i>P</i> Branch	340	1866.5	23.2
" " " <i>Q</i> "	350	1889.7	
" " " <i>R</i> "	360	1913.5	
Maximum of Envelope, <i>P</i> Branch	440	2023.2	23.8
" " " <i>Q</i> "	450	2047.0	
" " " <i>R</i> "	460	2070.6	

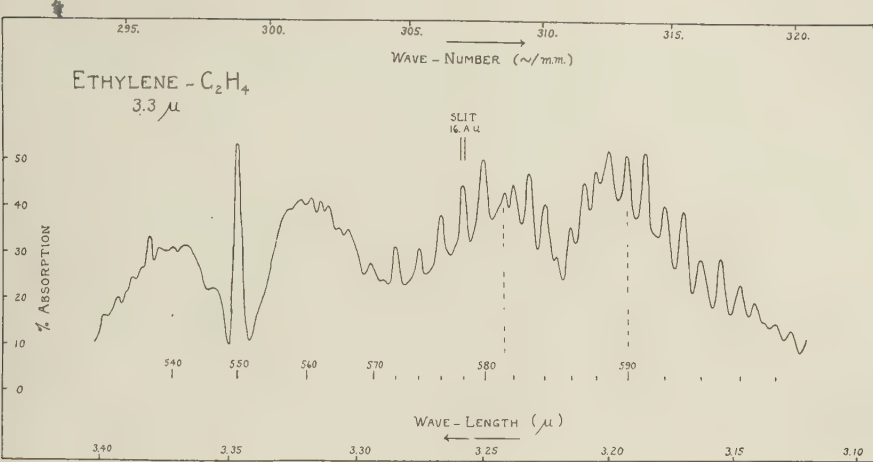


FIG. 8.

TABLE 8. Ethylene—Region of 3.3μ.

Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$
570	3036.5		581	3084.9		587	3115.8		593	3154.7	
		8.4			3.5			4.7			6.0
2	44.9		2	88.4		8	20.5		4	60.7	
		7.5			6.0			4.5			8.6
4	52.4		3	94.4		9	25.0		5	69.3	
		8.5			5.6			7.4			8.0
6	60.9		4	3100.0		590	32.4		6	77.3	
		8.6			4.3			7.2			5.9
8	69.5		5	04.3		1	39.6		7	83.2	
		8.3			6.5			7.8			
580	77.8		6	10.8		2	47.4				
		7.1			5.0			7.3			

	Line no.	ν /cm	$\Delta\nu$
Maximum of Envelope, P Branch	540	2965.9	
" " " Q "	550	2988.2	22.3
" " " R "	560	3012.6	24.4
Maximum of Envelope, P Branch	581	3084.9	
Minimum of Envelope; Band Center		3107.4	22.5
Maximum of Envelope, R Branch	590	3132.4	25.0

shown by the tabulated values 44.1, 47.0, and 47.4 cm^{-1} . The curves given for the three regions were obtained with different amounts of gas in the absorption chamber, hence no comparisons of relative intensities of the bands should be attempted.

Several efforts have been made to resolve the individual lines of the band at 6.9μ , but the curve shown in the figure represents the best definition attained. Apparently the structure in this region is too fine to be fully resolved by slit widths of 60A with reading intervals of $\frac{1}{2}$ minute of arc. The marked irregularities in the *R* branch are to a great extent attributable to the water vapor in the atmosphere. The fine structure of the strong band of water vapor in this region tends to falsify the absorption percentages obtained for the ethylene gas. At

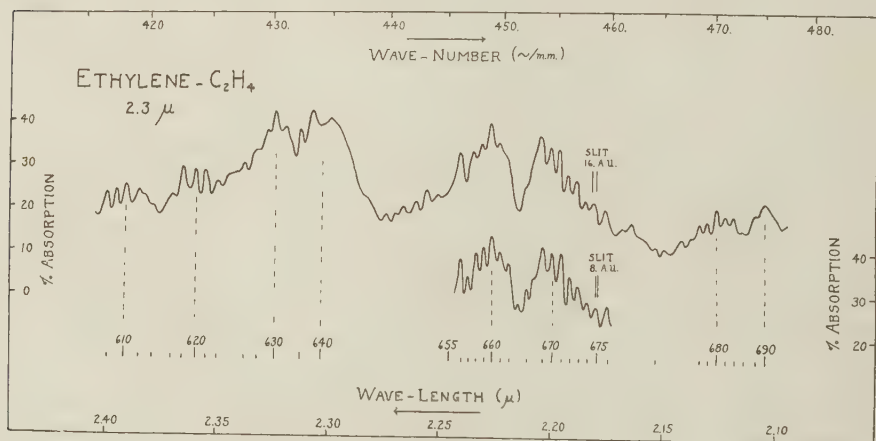


FIG. 9.

the extreme left end of the *P* branch four lines have been separated, and their positions show an average spacing of approximately 3.6 cm^{-1} .

The band at 5.3μ exhibits an extremely narrow and well defined *Q* branch. Some indications of fine structure appear in the *P* branch but further resolution could not be obtained. In the direction of greater wave-lengths, the run was extended out far beyond 5.8μ without revealing any additional regions of absorption. It is true that pronounced irregularities in the curve were noted in the region of 6.0μ , but these are quite evidently due to experimental error introduced by the strong band of water vapor in the atmosphere.

As the absorption at 4.9μ is very low, it was found necessary to increase the gas content of the cell in order to obtain the curve as shown

TABLE 9. *Ethylene—Region of 2.3μ.*

Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$
608	4165.6	7.8	656	4460.7	6.4	665	4512.4	7.8	674	4575.8	8.8
609	73.4		7	67.1		6	20.2		5	84.6	
610	81.3	7.9	8	73.7	6.6	7	27.3	7.1	6	95.4	10.8
618	4226.7	9.9	9	81.1	7.4	8	34.7	7.4	8	4684.9	8.6
620	36.6		660	87.9		670	43.4		9	93.5	
622	45.2	8.6	2	95.8	7.9	1	51.4	8.0	680	4702.1	8.6
624	55.0	9.8	4	4503.7	7.9	2	59.5	8.1	2	10.8	8.7
					8.7	3	67.7	8.2	4	18.8	8.0
								8.1			

	Coinciding with line no.	Wave number ν /cm	$\Delta\nu$
Maximum of Envelope, <i>P</i> Branch	610	4181.3	26.6
Minimum of Envelope; Band Center		4207.9	
Maximum of Envelope, <i>R</i> Branch	620	4236.6	28.7
Maximum of Envelope, <i>P</i> Branch		4302.2	
Minimum of Envelope; Band Center	630	4324.3	22.1
Maximum of Envelope, <i>R</i> Branch		4341.2	
Maximum of Envelope, <i>P</i> Branch	640	4487.9	16.9
Minimum of Envelope; Band Center		4515.5	
Maximum of Envelope, <i>R</i> Branch	660	4543.4	27.6
Maximum of Envelope, <i>P</i> Branch		4702.1	
Minimum of Envelope; Band Center	670	4729.0	27.9
Maximum of Envelope, <i>R</i> Branch		4750.1	
Maximum of Envelope, <i>P</i> Branch	680	4729.0	26.9
Minimum of Envelope; Band Center		4729.0	
Maximum of Envelope, <i>R</i> Branch	690	4750.1	21.1
Maximum of Envelope, <i>P</i> Branch		4750.1	

in the figure. Here we again see evidences of incompletely resolved fine structure in the P branch.

Region of 3.3μ (Fig. 8, Table 8): This is a double band, the first member of which consists of P , Q , and R branches and is centered at 3.35μ . The second band has P and R branches only and lies in the neighborhood of 3.22μ . The fine structure for the latter band has been resolved, the positions of some twenty-three lines being tabulated. In the P branch the spacing is fairly regular between lines 572 and 580, the average $\Delta\nu$ being 8.3 cm^{-1} . Between lines 580 and 589 the structure is more obscure, but it is again clear toward the right end of the R branch. Here the average $\Delta\nu$ is 7.5 cm^{-1} (from lines 589 to 596).

The doublet separation of the band at 3.35μ is taken as 46.7 cm^{-1} . This value is apparently identical with that obtained for the three bands shown in the previous figure. A value of 47.5 cm^{-1} is tabulated for the doublet at 3.22μ .¹¹ Due to the nature of the envelope, considerable latitude is possible here in the choice of the maxima.

Region of 2.3μ (Fig. 9, Table 9): The simple absorption maximum shown by Coblentz resolves into two intense doublets flanked by a faint doublet on each side. In other words, there apparently are in this region four distinct bands, each consisting of P and R branches only. The doublet separations as recorded in the table are 55.3, 39.0, 55.5, and 48.0 cm^{-1} . For convenience in distinguishing between the four bands, they will be referred to in the following discussion as the 2.4, 2.3, 2.2, and 2.1μ bands respectively.

The complete run, which is represented, was taken at intervals of one minute of arc. The band at 2.2μ was subsequently re-examined at intervals of one-half minute of arc and with a slit width of $8A$. With the consequently improved definition the small detached curve shown in the figure was obtained. The absorption scale for this curve is found at the right side of the figure. The best defined lines have a spacing of about eight waves per centimeter. The spacing of the few lines obtained in the 2.1μ and the 2.3μ bands does not differ greatly from this value, nor does that of the 3.22μ band. In the 10.5μ band the spacing in the P branch is somewhat smaller, and between intense lines in the R branch it is somewhat greater. It may be that there is a

¹¹ This value is larger than the doublet separation of 42.6 cm^{-1} which was previously obtained from the unresolved band (see footnote 1).

common predominant spacing in all of the bands of ethylene which have been resolved into lines. In the bands which have not been resolved, the spacings must be much smaller.

ETHANE

The three principal regions of absorption shown by Coblenz have been investigated, together with the minor region at 2.4μ . The work of Coblenz indicates that the two remaining absorption maxima in the vicinities of 8μ and 10μ are due to impurities in the gas used, and hence these regions were not examined.

The ethane gas was furnished in a cylinder by the Carbide and Carbon Chemicals Corporation. The purity was stated to be 90 per cent, the balance being specified as methane or propane or both.

The features introduced into the curves by the presence of methane as impurity in the gas can be easily detected, as the spectrum of methane is well known. Attention will be called to them in the proper places. The effects caused by propane, if present, are more troublesome to determine as its spectrum is not known. Therefore, some runs were made with propane in the cell by way of control. The propane was also obtained from the Carbide and Carbon Chemicals Corporation who state that the purity is 97 per cent, the balance being ethane and butane. The control runs show that propane has regions of absorption which overlies very closely the 6.8μ , 3.4μ , and 2.4μ regions of ethane. There is little or no absorption due to propane at 12.2μ , where ethane has intense absorption.

The curves obtained for propane not only overlies those for ethane in the three regions above mentioned, but they bear a very striking resemblance to them. The two sets of curves have many features in common, which occur in both sets in the same spectral position and with about the same intensity. However, if any of the features in the curves obtained for ethane were due primarily to the presence of propane as impurity, these features should appear greatly intensified in the curves obtained when the cell was filled with propane. Such intensification was nowhere found. The presumption is, therefore, that the curves for ethane are not markedly affected by the impurity of propane which may be present. It would perhaps have been better to have purified the ethane by fractional distillation. But the above mentioned control runs would have been necessary even then, and it is believed that these runs furnish fairly conclusive evidence in themselves.

Region of 12.2 μ (Fig. 10, Table 10): This band shows a single succession of absorption maxima which increase in intensity as the center of the band is approached. Such a series of maxima has been previously found for ammonia and has been interpreted as a series of *Q* branches.¹²

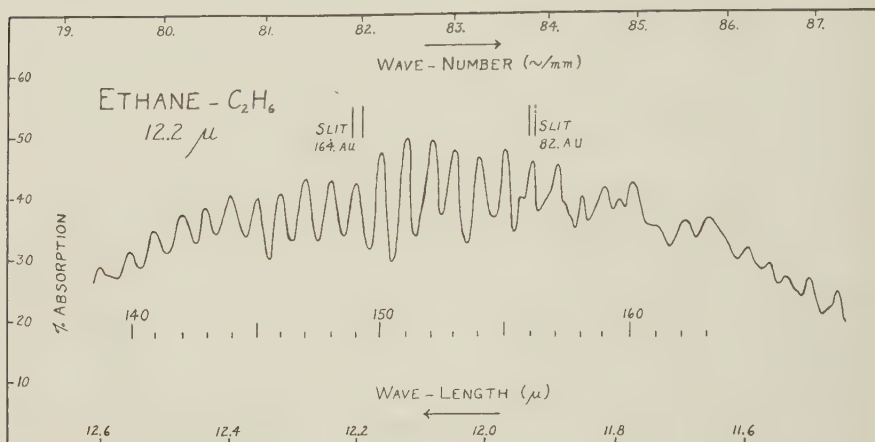


FIG. 10.

TABLE 10. *Ethane—Region of 12.2 μ .*

Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$
140	796.46		145	809.15		151	824.67		156	838.21	
		2.43			2.53			2.81			2.75
1	798.89		6	811.68		2	827.48		7	840.96	
		2.78			2.54			2.40			2.73
2	801.67		7	814.22		3	829.88		8	843.69	
		2.42			2.62			2.68			2.43
3	804.09		8	816.84		4	832.56		9	846.12	
		2.51			2.58			2.80			
4	806.60		9	819.42		5	835.36				
		2.55			2.64			2.85			
			150	822.06							
					2.61						

The spacing of the maxima obtained for ethane is regular between 11.8 μ and 12.6 μ . To both sides of this region the structure becomes more obscure as the absorption decreases. To the right of the line numbered

¹² Colby, W. F. and Barker, E. F. *Physical Review*, 29, p. 923; 1926.

150, the increased energy available permitted a decrease in the slit widths, thus improving the definition. This improvement, however, did not offer sufficient resolution to clear up the portion of the curve

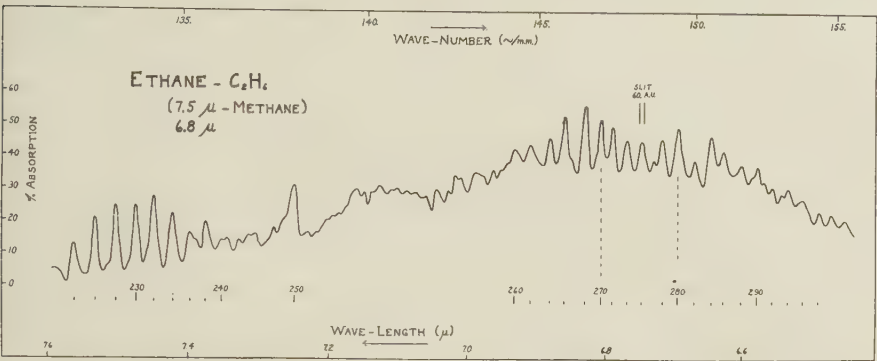


FIG. 11.

TABLE 11. Ethane—Regions of 7.5, 6.8μ.

Line no.	Wave no. ν /cm	$\Delta\nu$	Cooley, methane lines	Line no.	Wave no. ν /cm	$\Delta\nu$	Line no.	Wave no. ν /cm	$\Delta\nu$
224	1322.5		1323.0	260	1442.5		276	1482.3	
		5.1				4.9			4.2
6	27.6		28.3	2	47.4		7	86.5	
		5.1				5.7			2.4
8	32.7		33.3	4	53.1		8	88.9	
		5.1				5.0			5.2
230	37.8		38.3	6	58.1		280	94.1	
		4.6				6.2			5.5
2	42.4		42.9	8	1464.3		2	99.6	
		4.9				4.9			5.5
4	47.3		47.8	270	69.2		4	1505.1	
		4.4				4.1			4.2
6	51.7		52.5	2	73.3		6	09.3	
		4.1				4.3			6.3
8	55.8		56.7	4	77.6		8	15.6	
						4.7			
250	1379.4								

at the right of the figure, which remains incompletely resolved. At the left end, the curve was extended far beyond 13.3μ without revealing anything of further interest.

The fine structure obtained between lines 140 and 159 yields an average $\Delta\nu$ of 2.6 cm^{-1} . The spacing of the lines in this region shows a slight convergence in the direction of lower wave-numbers.

Region of 6.8μ (Fig. 11, Table 11): The absorption curve reveals regular structure between 6.6 and 6.9μ and again between 7.4 and 7.6μ , with more complicated structure in the intervening region. The band at 6.8μ corresponds to the sharp absorption maximum shown by Coblenz in his prism curve for ethane. It yields an average spacing of approximately 4.9 cm^{-1} between successive lines.

The eight sharply defined lines occurring in the 7.5μ region are definitely assignable to the impurity of methane contained in the gas. The positions of these eight lines, as computed by Cooley in his investigation of methane,¹³ are included in Table 11 for purposes of comparison. It is seen that each position checks the value obtained in the present work within about 0.5 cm^{-1} .

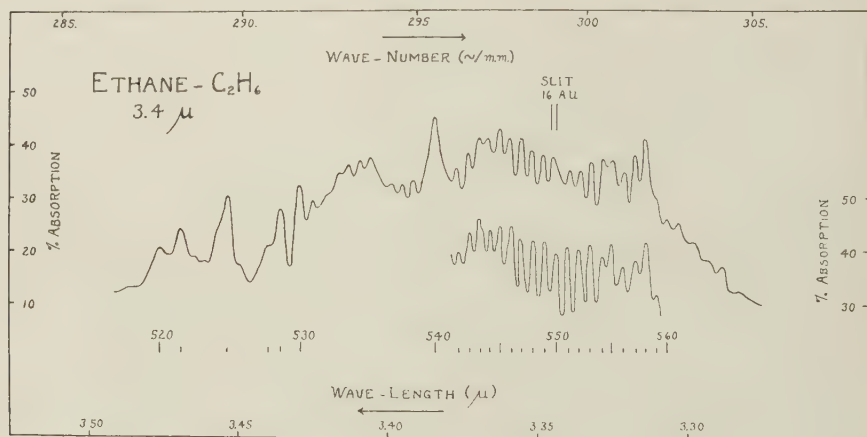


FIG. 12.

Since the absorption of methane is practically negligible between 6.9 and 7.4μ , the complexity of the structure in this region cannot be attributed to the impurity of methane. The presence of propane, on the other hand, would undoubtedly be a complicating factor, but would not account for such prominent features as the No. 250 line in the ethane curve. This absorption maximum apparently belongs to the spectrum of ethane.

Region of 3.4μ (Fig. 12, Table 12): A run was taken over this region at one minute intervals of arc and this was supplemented by a run at

¹³ Cooley, J. P. *Astrophysical Journal*, 62, pp. 73-83; 1925.

one-half minute intervals over a portion of the curve. This supplementary run shows a regular spacing which averages 3.3 cm^{-1} between lines 541 and 559. A slight convergence again exists in the direction of lower wave-numbers.

TABLE 12. *Ethane—Region of 3.4μ .*

Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$	Line no.	Wave no. ν/cm	$\Delta\nu$
522	2882.5		542	2965.2		548	2983.8		554	3004.4	
					2.9			3.3			2.7
524	2895.5		3	68.1		9	87.1		5	07.1	
					3.0			3.5			3.7
528	2910.9		4	71.1		550	90.6		6	10.8	
					3.1			3.5			3.7
530	16.3		5	74.2		1	94.1		7	14.5	
					3.2			3.4			3.0
540	54.8		6	77.4		2	97.5		8	17.5	
					2.8			3.2			3.1
541	61.9		7	80.2		3	3000.7		9	20.6	
		3.3			3.6			3.7			

The prominent features of the main curve for the 3.4μ region may safely be ascribed to ethane, as the propane band does not exhibit maxima corresponding to lines 524 and 540. The effect of the impurity of methane is slightly noticeable in the region between lines 553 and 558. Here the shape of the envelope for the ethane curve is distorted by the superposed *Q* branch of methane.

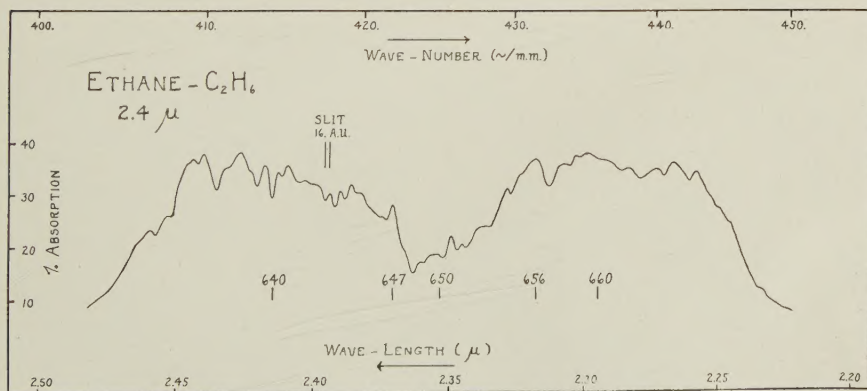


FIG. 13.

Region of 2.4μ (Fig. 13): The curve shows two main regions of absorption, the approximate maxima of which are separated by 220 cm^{-1} . An additional run taken over a portion of the curve at one-half minute intervals and with slits of 8A revealed no evidence of uniform or simple fine structure. The lines numbered 647 and 656 coincide in position with absorption maxima of methane tabulated by Cooley.

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DECEMBER, 1927.

